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Structural phase transitions and dielectric transitions in a 1,4-diazabicyclo[2.2.2]octane (dabco) based organic crystal

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ABSTRACT

1,4-Diazabicyclo[2.2.2]octane (dabco) based organic crystal [(Hdabco)(H_2O)](PF_6) (**1**) was synthesized and characterized. Its structure is featured by wavy-like one-dimensional supramolecular hydrogen bond chains built from the [(Hdabco)(H_2O)] units from end to end. Compound **1** undergoes two reversible phase transitions at 226/268 K and 178/181 K, respectively. The disorder-order transition of water molecule in the hydrogen bond chain induces the phase transition at 226 K while the twisting of the $[Hdabco]^+$ cation and displacements of the PF_6^- anion and H_2O molecules trigger the phase transition at 178 K. Dielectric transitions are thus triggered in the crystal.

1. Introduction

Structural phase transitions in solid-state materials often trigger striking changes of physical and chemical properties to result in useful materials [1–6]. One example is dielectric transition or switchable dielectric constant that is a switching property in molecule-base materials in which the dielectric constant can be switched between high- and low-state under external stimuli [7–14]. This property mainly arises from the dynamic changes of polar molecules or ions in the crystal lattices between static (ordered) and dynamic (disordered) states. However, to predict and design the switchable dielectric constants in crystals is very challenging because the lack of deep understanding of interionic and/or intermolecular interactions in crystals that determine the occurrence of phase transitions and the corresponding dielectric transitions [15]. So it is necessary to perform studies on new phase transition compounds to gain new insight into the structure-property relationship of solid-state phase transitions and dielectric transitions.

1,4-Diazabicyclo[2.2.2]octane (dabco) is a very useful organic component in building phase transition crystals because of its highly symmetric shape that tends to undergo order-disorder transformations in crystals and its multiple roles in formation of hydrogen bonds by acting either H donor or acceptor or both [16–30]. Herein, we report a new mono-protonated dabco based organic salt [(Hdabco)(H_2O)](PF_6) (**1**), which contains wavy-like 1D supramolecular hydrogen bond chains based on the [(Hdabco)(H_2O)] unit. The crystal displays two reversible phase transitions at 226/268 K and 178/181 K with different structural origins, i.e., the disorder-order transition of water molecule in the hydrogen bond chain for the former phase transition while the twisting of the $[Hdabco]^+$ cation and displacements of the PF_6^- anion and H_2O molecules for the latter phase transition. A dielectric transition occurs during the lower-temperature phase transition. The title compound affords an example of molecule-based switchable dielectric crystals with a simple composition but showing relatively complex phase transitions.

2. Experimental section

2.1. Materials and methods

All the analytical grade chemicals were used as received without further purification. Elemental analysis was performed on a vario MICRO analyzer. Infrared (IR) spectra were recorded on a Nicolet 5700 spectrometer. Raman spectra were measured on Thermo Fisher spectrometer. Thermogravimetric analysis (TGA) was carried

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out on a METTLER TOLEDO STARe System. Measurements of differential scanning calorimetry (DSC) were performed on a Perkin-Elmer Diamond DSC instrument from 130 to 293 K and the heating rate is 10 K/min at atmospheric pressure. Powder X-ray diffraction (PXRD) was measured on a Rigaku SmartLab X-ray diffraction instrument. Dielectric measurements were performed on a TongHui 2828 impedance Analyzer over the frequency range from 500 Hz to 1 MHz and the temperature range from 120 K to 300 K with an applied electric field of 1.0 V.

2.2. Synthesis of compounds 1 and 2

Dabco (1.1217 g, 10 mmol) and 60% hexafluorophosphate acid (2.43 g, 10 mmol) were mixed in water (15 ml). Evaporation of the solution at room temperature for several days yielded colorless sheet-like crystals of **1** with a yield of 81%. Crystals of **2** were obtained through re-crystallizing **1** in D_2O by five times. Elemental analysis calcd (%) for **1** [$C_6H_{15}F_6N_2OP$ (276.083)]: C 26.10, H 5.47, N 10.14; found: C 26.28, H 5.43, N 10.13. **2** [$C_6H_{12}D_3F_6N_2OP$ (276.101)]: C 25.81, N 10.03; found: C 26.28, N 9.96.

2.3. Crystal structure measurement

Single-crystal data of **1** were collected at different temperatures on a Rigaku Saturn 724$^+$ diffractometer equipped with a Rigaku low-temperature gas spray cooler device by using Mo-Kα (λ = 0.71075 Å) radiation from a graphite monochromator. Data processing was performed using the CrystalClear software package (Rigaku, 2005). The structures were solved by direct methods and successive Fourier synthesis and then refined by full-matrix least-squares refinements on F^2 using the SHELXL-2014 software package [31]. Hydrogen atoms bonded to the carbon atoms were placed in calculated positions and refined as a riding mode, with C–H = 0.96 Å (methylene) with U_{iso}(H) = 1.2 U_{eq}(C). Summary of crystallographic data for the compounds are given in Table 1. CCDC 1436110-1436112 contain the supplementary crystallographic data for **1**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

3. Results and discussion

3.1. Thermal analysis

Phase transitions of **1** are confirmed by DSC measurement between 120 and 293 K (Fig. 1). Two reversible phase transitions were found at 226/268 K and 178/181 K, respectively, upon cooling and heating. For convenience, phase I, II and III are assigned to the phase above 226 K, between 226 K and 178 K, and below 178 K, respectively. It is noted the I-II phase transition displays a large thermal hysteresis of about 42 K. For the deuterated compound **2**, the I-II phase transition occurs at 237 K upon cooling, showing an obvious deuterium isotope effect with a temperature upshift of about 11 K. It indicates that this phase transition has a relation with the proton, which is similar with the phase transitions in some hydrogen bond ferroelectrics [5].

3.2. Crystal structures

The basic structural unit of **1** contains one [Hdabco]$^+$ cation, one PF_6^- anion and one H_2O molecule at 273 K and 200 K (Fig. 2). The water molecule shows a disorder over two sites at 273 K and

Table 1
Crystallographic data and structural refinement details for **1**.

T/K	273(2)	200(2)	93(2)
Formula	$C_6H_{15}F_6N_2OP$	$C_6H_{15}F_6N_2OP$	$C_6H_{15}F_6N_2OP$
Formula weight	276.17	276.17	276.17
Crystal system	orthorhombic	orthorhombic	monoclinic
Space group	*Pnma*	*Pnma*	$P2_1/c$
a/Å	11.852(9)	11.840(7)	8.948(5)
b/Å	9.062(7)	8.999(6)	30.04(2)
c/Å	10.238(8)	10.167(6)	11.856(7)
α/°	90	90	90
β/°	90	90	90.416(9)
γ/°	90	90	90
V/Å^3	1099.6(15)	1083.3(12)	3187(3)
Z	4	4	12
D_{calc}/g cm^{-3}	1.668	1.693	1.727
μ/mm^{-1}	0.316	0.321	0.327
F(000)	568	568	1704
θ range/°	3.460–27.465	3.441–27.468	3.167–27.448
Reflns collected	11355	11115	32974
Independent reflns (R_{int})	1341(0.0496)	1322 (0.0341)	7296(0.0534)
No. parameters	95	85	469
R_1[a], wR_2[b] [$I > 2\sigma(I)$]	0.0719, 0.1845	0.0519, 0.1348	0.0688, 0.1437
R_1, wR_2 [all data]	0.0842, 0.1930	0.0565, 0.1377	0.0915, 0.1544
GOF	1.132	1.095	1.137
$\Delta\rho$[c]/e•Å^{-3}	0.364, −0.333	0.320, −0.281	0.619, −0.416

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.
[c] Maximum and minimum residual electron density.

becomes ordered at 200 K. The unit cell is tripled from 1083.3 Å^3 in phase II to 3187 Å^3 in phase III during the II-III phase transition (Table 1) [9]. In phase III there are three [(Hdabco)(H_2O)](PF_6) basic units in the cell unit.

Crystal **1** displays one-dimensional (1D) hydrogen bond chains in all the three phases (Fig. 3a). The water molecule connects the mono-protonated dabco via hydrogen bonds. It accepts the hydrogen atom from the N–H to form the N–H···O hydrogen bond and donates its two hydrogen atoms to one F atom in the anion and one un-protonated N atom in the cation to form O–H···F and O–H···N hydrogen bonds, respectively. The solvent molecules act as nodes to connect the PF_6^- anions and [Hdabco]$^+$ cations in the hydrogen bond chain. The [(Hdabco)(H_2O)] units form a wavy-like 1D supramolecular hydrogen bond chain from end to end, which is closely related to the characteristic linear 1D N–H···N hydrogen bond chains in the (Hdabco)X (X = ClO_4^-, BF_4^-, ReO_4^-, etc) compounds [24,27]. The [Hdabco]$^+$ cations in **1** have two orientations in

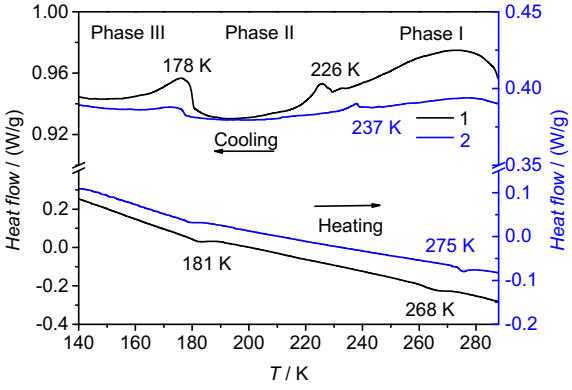

Fig. 1. DSC curves of **1** and **2**.